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(54) Title: LIQUID DETERGENTS (57) Abstract <p>A detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase, said composition comprising from 0.1 to 16 % by weight of surface active materials and no or less than 20 % by weight of STP plus zeolite builder material, said composition also comprising a deflocculating polymer; with the provisos that (a) when the level of surface active materials is between 12 % and 16 % by weight of the composition, then the composition comprises no or less than 7 % by weight of STP plus zeolite builder material; and (b) when the composition comprises from 3 % to 12 % of a potassium alkyl benzene sulphonate, from 2 % to 8 % of a potassium fatty acid soap, from 0.5 to 5 % of a nonionic surfactant, and from 1 to 25 % of STP and/or tetrapotassium pyrophosphate, all percentages being by weight, the weight ratio of said sulphonate to said nonionic surfactant being from 3:5 to 25:1, and the total amount of said sulphonate, soap and nonionic surfactant being from 7.5 to 20 % by weight, then the deflocculating polymer does not consist solely of from 0.1 to 2 % by weight of a partially esterified, neutralised copolymer of maleic anhydride with vinylmethyl ether, ethylene or styrene.</p>		

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LIQUID DETERGENTS

The present invention is concerned with aqueous detergent compositions which contain sufficient detergent-active material and, optionally, sufficiently dissolved electrolyte to result in a structure of lamellar droplets dispersed in a continuous aqueous phase. In particular the present invention relates to liquid detergent compositions which contain low levels of detergent active materials.

Lamellar droplets are a particular class of surfactant structures which, inter alia, are already known from a variety of references, e.g. H.A.Barnes, 'Detergents', Ch.2. in K.Walters (Ed), 'Rheometry: Industrial Applications', J. Wiley & Sons, Letchworth 1980.

Such lamellar dispersions are used to endow properties such as consumer-preferred flow behaviour and/or turbid appearance. Many are also capable of suspending particulate solids such as detergency builders or abrasive particles. Examples of such structured liquids without suspended solids are given in US patent 4 244 840, whilst examples where solid particles are suspended are disclosed in specifications EP-A-160 342; EP-A-38 101; EP-A-104 452 and also in the aforementioned US 4 244 840. Others are disclosed in European Patent Specification EP-A-151 884, where the lamellar droplet are called 'spherulites'.

The presence of lamellar droplets in a detergent product may be detected by means known to those skilled in the art, for example optical techniques, various rheometrical measurements. X-ray or neutron diffraction, and electron microscopy.

5 The droplets consist of an onion-like configuration of concentric bi-layers of surfactant molecules, between which is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties.

10 The viscosity and stability of the product depend on the volume fraction of the product which is occupied by the droplets. Generally speaking, when the volume fraction is around 0.6, the droplets are just touching (space-filling). This allows reasonable stability with an
15 acceptable viscosity.

Detergent products for use on hard surfaces tend to contain relatively low levels of surfactant materials, say from 0.1 to 16 % weight of the compositions. These
20 low levels of surface-active ingredients sometimes render it difficult to formulate detergent compositions of the lamellar droplet-type. Often products containing these low active levels are not entirely stable and/or have an unacceptable low viscosity.

25 For overcoming these problems, it has hitherto been customary to add one or more thickening ingredients and/or one or more external structurants to these compositions. These solutions are, however, not
30 entirely satisfactory, because they sometimes only allow the formulation of the product within narrow boundaries, also the use of separate thickener and/or structuring ingredients is often less preferred because of processing difficulties.

35

Surprisingly it has now been found that an increased flexibility in formulating detergent compositions of the lamellar droplet type, and containing only relatively low active levels and/or an increased viscosity of said compositions can be obtained by incorporating therein a so-called deflocculating polymer.

The use of deflocculating polymers in liquid detergent compositions of relatively high active levels and/or high levels of phosphate or zeolite builders is already described in our non-prepublished european patent application EP 89201530.6 (EP 346 995) and Brithish patent applications 8924479.2, 8924478.4 and 8924477.6. The compositions as disclosed in these applications comprise generally high levels (about 17 weight % or more) of surface active ingredients and/or high total levels of STP plus zeolite; or they comprise somewhat lower levels of active material in the presence of at least 8 % by weigth of STP. Compositions as disclosed in these patent applications are herewith disclaimed from the scope of the present invention.

It has also been suggested in GB 1,506,427 to formulate liquid detergent compositions containing five essential ingredients in specific relative amounts. The compositions described contain from 3-12 % by weight of a potassium alkylbenzenesulphonate, 2-8 % by weight of a potasssium soap of a C₈-22 fatty acids or polymers thereof and 0.5 to 5 % by weight of a nonionic

detergent active material, wherein the relative ratios of the active ingredients are within narrowly defined ranges. Compositions according to this patent comprise from 1-25 % of an alkali metal tripolyphosphate and from 0.1-2 % of a specific copolymer of maleic anhydride with vinylmethylether, ethylene or styrene, partially esterified with the nonionic detergent active material.

GB 1,589,971 relates to similar compositions wherein part of the alkali metal tripolyphosphate is replaced by tetrapotassium pyrophosphate. The compositions according to the two above mentioned British patents are hereby
5 disclaimed from the scope of the present invention.

Accordingly the present invention relates to a detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous
10 phase, said composition comprising from 0.1 to 16 % by weight of surface active materials and no or less than 20 % by weight of STP plus zeolite builder material, said composition also comprising a deflocculating
polymer ;

15

with the provisos that

(a) when the level of surface active materials is between 12 % and 16 % by weight of the composition,
20 then the composition comprises no or less than 7 % by weight of STP plus zeolite builder material; and

(b) when the composition comprises from 3 % to 12 % of a potassium alkyl benzene sulphonate, from 2 % to 8 % of a
25 potassium fatty acid soap, from 0.5 to 5 % of a nonionic surfactant, and from 1 to 25 % of STP and/or tetrapotassium pyrophosphate, all percentages being by weight, the weight ration of said sulphonate to said nonionic surfactant being from 3:5 to 25:1, and the
30 total amount of said sulphonate, soap and nonionic surfactant being from, 7.5 to 20 % by weight,

then the deflocculating polymer does not consist solely of from 0.1 to 2% by weight of a partially esterified,
35 neutralised co-polymer of maleic anhydride with vinylmethyl ether, ethylene or styrene.

Without being bound by any particular interpretation or theory, it is hypothesised that the deflocculating polymers exert their action on the composition by the following mechanisms.

First the polymers will possibly at least partly be incorporated inside the droplets, this has the effect of decoupling the inter- and intra-droplet forces, i.e. the difference between the forces between individual surfactant molecules in adjacent layers within a particular droplet and those between surfactant molecules in adjacent droplets could become accentuated, in that the forces between the adjacent droplets are reduced. This will possibly lead to increased stability and less flocculation, especially at high electrolyte levels.

The influence of these polymers within the droplets on the viscosity is governed by two opposite effects : firstly the presence of decoupling polymers will decrease the forces between adjacent droplets resulting in greater distances between the droplets, generally resulting in a lower viscosity and a better stability of the system; secondly the forces between the layers within the droplets are equally reduced by the presence of the polymers in the droplet, this generally result in an increase in the lamellar water-layer thickness, therewith increasing the lamellar volume of the droplets, therewith increasing the viscosity. The net effect of these two opposite effects in systems of low active level is most likely an increase in the viscosity of the product.

Secondly, when deflocculating polymers comprising two groups which may be linked to the lamellar droplets are

used, then the polymer may actually form a linkage between two or more lamellar droplets, whereby an additional structure may be formed which provides a thickening effect.

5

Preferably compositions of the invention are physically stable. In the context of the present invention, physical stability for these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more 10 %, preferably no more than 5 %, most preferred no more than 2% by volume phase separation as evidenced by appearance of 2 or more separate phases when stored at 25°C for 21 days from the time of preparation. Especially interesting is the use of deflocculating polymers in compositions which are unstable in the absence of deflocculating polymer, but stable in the presence of said polymer.

20

Compositions of the invention may be pourable liquids, but also possible are products in gel or paste-form.

25

Gel or paste compositions according to the invention preferably have a viscosity of between 2,000 and 20,000 mPas at 21 s⁻¹, more preferred between 5,000 and 15,000, most preferred from 8,000 to 12,000.

30

Liquid compositions of the invention preferably have a viscosity of less than 2,500 mPas at 21 s⁻¹ and more than 25 mPas at 21 s⁻¹, more preferred less than 2,000 mPas and more than 50 mPas, most preferred less than 1,500 mPas and more than 100 mPas, e.g about 1,000 mPas.

35

Preferably compositions of the invention are more viscous than a corresponding composition without the

deflocculating polymer. Preferably the increase of viscosity by adding the polymer at a level of 1.0 wt % is at least 10 %, more preferred more than 20 %, especially preferred more than 35 %.

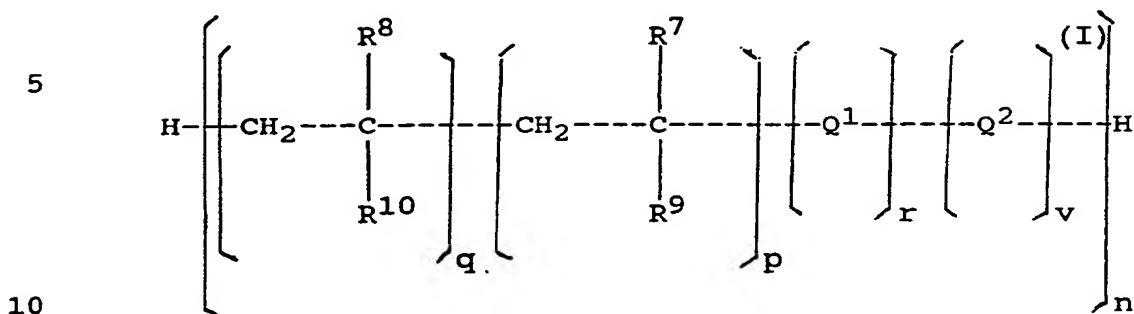
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Suitable deflocculating polymers for use in compositions of the present invention are for instance described in our copending European patent application 89201530.6 (EP 346 995), polymers as described in this patent have a hydrophilic backbone and at least one hydrophobic side chain. Generally the hydrophilic backbone of the polymer is predominantly linear (the main chain of the backbone constitutes at least 50 %, preferably more than 75 %, most preferred more than 90% by weight of the backbone), suitable monomer constituents of the hydrophilic backbone are for example unsaturates C₁₋₆ acids, ethers, alcohols, aldehydes, ketones or esters, sugar units, alkoxy units, maleic anhydride and saturated polyalcohols such as glycerol. Examples of suitable monomer units are acrylic acid, methacrylic acid, maleic acid, vinyl acetic acid, glucosides, ethylene oxide and glycerol. The hydrophilic backbone made from the backbone constituents in the absence of hydrophilic side-groups is relatively water-soluble at ambient temperature and a pH of between 6.0 and 13.0. Preferably the solubility is more than 1 g/l, more preferred more than 5 g/l most preferred more than 10 g/l.

30 Preferably the hydrophobic sidegroups are composed of relatively hydrophobic alkoxy groups for example butylene oxide and/or propylene oxide and/or alkyl or alkenyl chains having from 5 to 24 carbon atoms. The hydrophobic groups may be connected to the hydrophilic backbone via relatively hydrophilic bonds for example a poly ethoxy linkage.

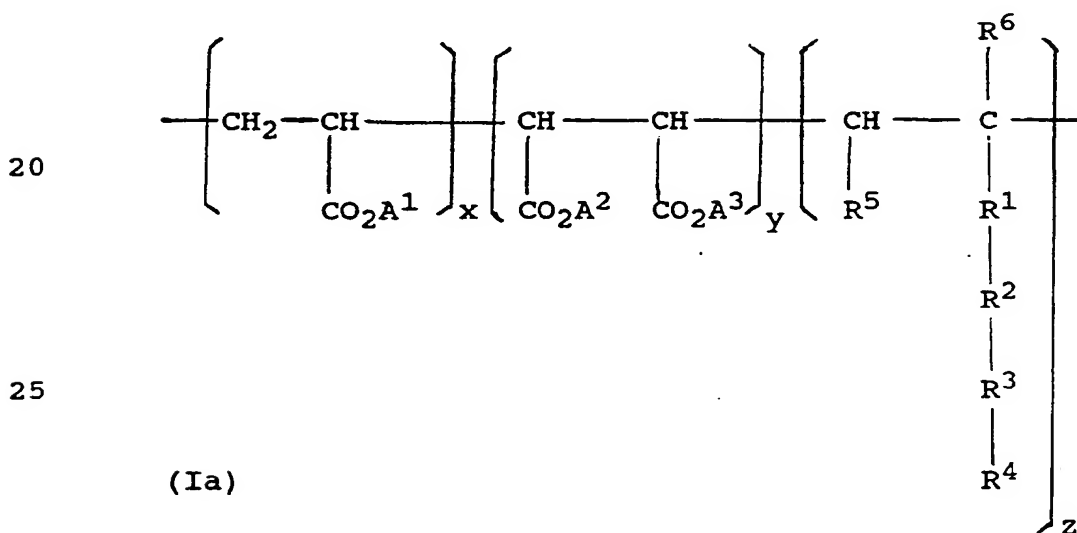
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Preferred polymers are of the formula:



Wherein:

Q^2 is a molecular entity of formula (Ia):



wherein:

R^1 represents $-\text{CO}-\text{O}-$, $-\text{O}-$, $-\text{O}-\text{CO}-$, $-\text{CH}_2-$, $-\text{CO}-\text{NH}-$ or is absent;

R^2 represents from 1 to 50 independently selected alkyleneoxy groups preferably ethylene oxide or

propylene oxide groups, or is absent, provided that when R^3 is absent and R^4 represents hydrogen or contains no more than 4 carbon atoms, then R^2 must contain an alkyleneoxy group preferably more than 5 alkyleneoxy groups with at least 3 carbon atoms;

R^3 represents a phenylene linkage, or is absent;

R^4 represents hydrogen or a C_{1-24} alkyl or C_{2-24} alkenyl group, with the provisos that

- a) when R^1 represents $-O-CO-$, R^2 and R^3 must be absent and R^4 must contain at least 5 carbon atoms;
- b) when R^2 is absent, R^4 is not hydrogen and when also R^3 is absent, then R^4 must contain at least 5 carbon atoms;

R^5 represents hydrogen or a group of formula $-COOA^4$;

R^6 represents hydrogen or C_{1-4} alkyl; and

A^1 , A^2 , A^3 and A^4 are independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and C_{1-4} , or $(C_2H_4O)_tH$ wherein t is from 1-50, and wherein the monomer units may be in random order.

Q^1 is a multifunctional monomer, allowing the branching of the polymer, wherein the monomers of the polymer may be connected to Q^1 in any direction, in any order,

therewith possibly resulting in a branched polymer. Preferably Q^1 is trimethyl propane triacrylate (TMPTA), methylene bisacrylamide or divinyl glycol.

n is at least 1; z and v are 1; and $(x + y + p + q + r)$: z is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1; in which the monomer units may be in random

order; and preferably either p and q are zero, or r is zero;

R⁷ and R⁸ represent -CH₃ or -H;

5

R⁹ and R¹⁰ represent substituent groups such as amino, amine, amide, sulphonate, sulphate, phosphonate, phosphate, hydroxy, carboxyl and oxide groups, preferably they are selected from -SO₃Na, -CO-O-C₂H₄-OSO₃Na, -CO-O-NH-C(CH₃)₂-SO₃Na, -CO-NH₂, -O-CO-CH₃, -OH;

10

Preferably polymers for use in compositions of the invention which are of relatively high pH (say 10 or more) are substantially free of hydrolysable groups such as carbonyl groups for increased polymer stability at high pH values. Particularly preferred polymers for use in high pH compositions of the invention comprise hydrophilic backbones constituted by acid groups such as acrylic acid and at least one hydrophobic side chain which is constituted of from 5 to 75 relatively water-insoluble alkoxy groups such as propoxy units optionally linked to the hydrophylic backbone via an -poly-alkoxy linkage constituted of from 1-10 relatively watersoluble alkoxy groups such as ethoxy units.

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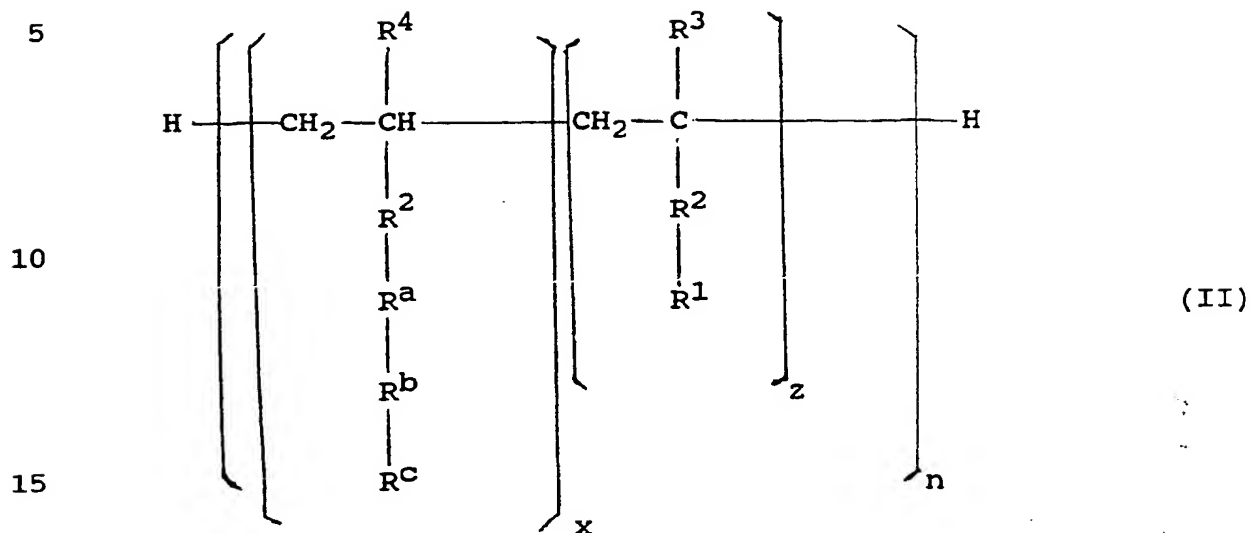
Other preferred polymers for use in compositions of the invention are described in our copending British patent applications 8924479.2, 8924478.4 and 8924477.6. Of the polymers described in those patent applications, especially the use of polymers in accordance with brithish patent application 8924478.4 is preferred.

30

These polymers are constituted of nonionic monomers and ionic monomers, wherein the ionic monomer is from 0.1 to 50 % by weight of the polymer. Especially preferred polymers of this type are of the formula:

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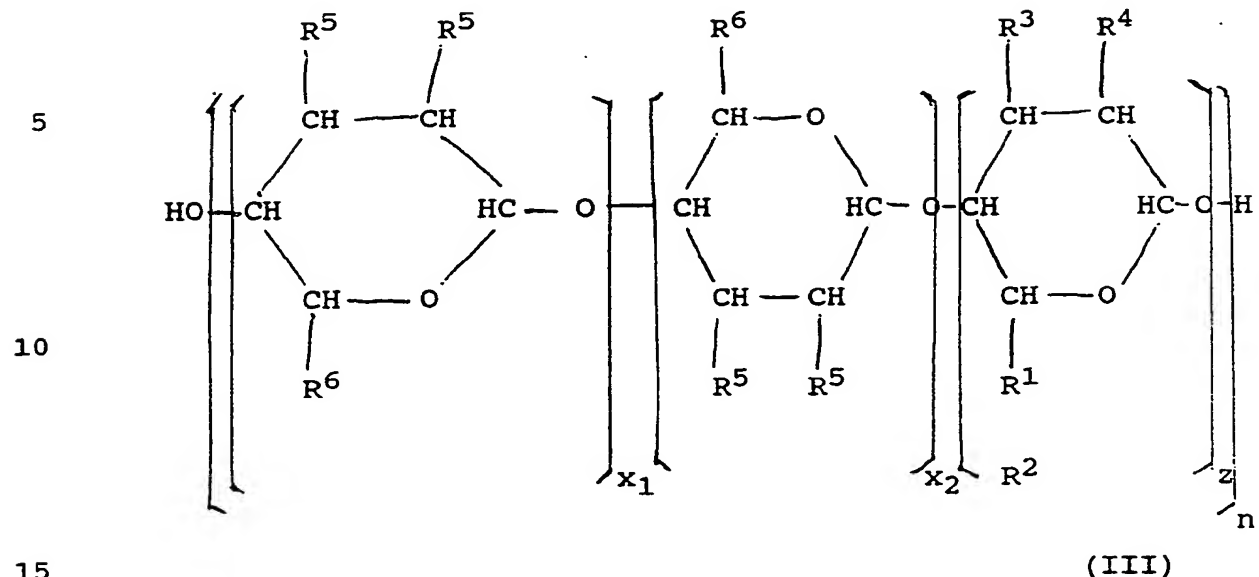
wherein: x, z and n are as above;

- R³ and R⁴ represent hydrogen or C₁₋₄ alkyl;
 - R² represents -CO-O-, -O-, -O-CO-,
-CH₂-, -CO-NH-, or is absent;
 - R¹ represents -C₃H₆-N⁺-(CH₃)₃(Cl⁻);
-C₂H₄-OSO₃⁻(Na⁺), -SO₃⁻(Na⁺),
-C₂H₄ N⁺(CH₃)₃ Cl⁻, -C₂H₄ N⁺ (C₂H₆)₃ Cl⁻,
-CH₂ N⁺ (CH₃)₃ Cl⁻, -CH₂ N⁺ (C₂H₆)₃ Cl⁻ or
benzyl-SO₃⁻ (Na⁺);
 - R^a is CH₂, C₂H₄, C₃H₆ or is absent;
 - R^b represents form 1 to 50 independently
selected alkylene oxide groups, preferably
ethylene oxide groups or is absent;
 - R^c represents -OH or -H;
- and wherein if R², R^a and R^b are absent, then R^c is not -H.

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Other preferred polymers have the formula:



Wherein:

- $x = x_1 + x_2$
- x, z and n are as defined above
- R^1 represents $-\text{CH}_2\text{O}-$ or $-\text{O}-$;
- R^2 represents $-\text{CH}_2\text{COO}^-\text{Na}^+$, $-\text{C}_3\text{H}_6\text{ON}^+(\text{CH}_3)_3\text{Cl}^-$ or $-\text{C}_3\text{H}_3\text{N}^+(\text{CH}_3)_3\text{Cl}^-$
- R^3 and R^4 represents $-\text{OH}$, CH_2OH , $-\text{O}(\text{C}_3\text{H}_6\text{O})_p-\text{H}$, $-\text{CH}_2-\text{O}(\text{C}_3\text{H}_6\text{O})_p-\text{H}$ or $-\text{OCH}_2\text{COO}^-\text{Na}^+$ or $-\text{O}-\text{C}_3\text{H}_6\text{ON}^+(\text{CH}_3)_3\text{Cl}^-$ or $-\text{O}-\text{C}_3\text{H}_6\text{N}^+(\text{CH}_3)_3\text{Cl}^-$
- R^5 represents $-\text{OH}$, $-\text{NH}-\text{CO}-\text{CH}_3$ or $-\text{O}(\text{C}_3\text{H}_6\text{O})_p-\text{H}$
- R^6 represents $-\text{OH}$, $-\text{CH}_2\text{OH}$, $-\text{CH}_2-\text{OCH}_3$, $-\text{O}(\text{C}_3\text{H}_6\text{O})_p-\text{H}$ or $-\text{CH}_2-\text{O}-(\text{C}_3\text{H}_6\text{O})_p-\text{H}$
- p is from 1 - 10.

Preferably polymers for use in compositions have a molecular weight (as determined as in our co-pending european patent application 89201530.6) of between 500 and 100,000, more preferred from 1,000 to 20,000, especially preferred from 1,500 to 10,000 most preferred

from 2,800 to 6,000. Polymers for use in compositions of the invention may for example be prepared by using conventional aqueous polymerisation procedures, suitable methods are for example described in the above mentioned co-pending European patent application.

Generally the deflocculating polymer will be used at from 0.01 to 5 % by weight of the composition, more preferably from 0.1 to 3.0, especially preferred from 0.25 to 2.0 %.

For obtaining the above described effect that polymers are incorporated in the lamellar droplets to increase the viscosity and/or the stability, especially the use of low molecular weight polymers is preferred, say less than 5,000, more preferred less than 3,500, most preferred between 500 and 2,000. Preferably the ratio of hydrophobic or ionic monomers to hydrophilic or nonionic monomers is from 1 : 1 to 1 : 100, preferably 1 : 4 to 1 : 25.

For obtaining the above described effect of linking one or more lamellar droplets it is preferred to use polymers comprising two or more hydrophobic or ionic monomers. Preferably polymers for this purpose are of relatively high molecular weight, say more than 2,000, preferably from 4,000 to 100,000, more preferred from 6,000 to 50,000. Also mixtures of relatively high mW polymers (say less than 5,000) and higher mW polymers (say above 5,000) may be used.

Compositions of the invention also comprise detergent active materials, preferably at a level of from 0.1 to 16% by weight of the composition, more preferred at a level of 2 to 12 % by weight, most preferred from 4 to 11 % by weight.

In the case of blends of surfactants, the precise proportions of each component which will result in lamellar structures will depend on the type(s) and amount(s) of the surfactants and the electrolytes (if present), as is the case with conventional structured systems such as liquids.

In the widest definition the detergent-active material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol.I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol.II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H.Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Preferably the level of nonionic surfactants is more than 0.2 % by weight of the composition, preferably from 0.5 to 6.0% by weight of the composition, more
5 preferred from 1.0 to 5.0 %.

Compositions of the present invention may contain synthetic anionic surfactant ingredients, which are preferably present in combination with the above
10 mentioned nonionic materials. Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon
15 atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by
20 sulphating higher (C₈-C₁₈) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C₉-C₂₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅)
25 benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium
coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C₈-C₁₈) fatty alcohol-alkylene
oxide, particularly ethylene oxide, reaction products;
30 the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine;
35 ~~alkane monosulphonates such as those derived by reacting~~
alpha-olefins (C₈-₂₀) with sodium bisulphite and those derived from reacting paraffins with SO₂ and Cl₂ and

then hydrolyzing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C₁₀-C₂₀ alpha-olefins, with SO₃ and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C₁₁-C₁₅) alkyl benzene sulphonates and sodium (C₁₆-C₁₈) alkyl sulphates.

Generally the level of the above mentioned anionic surfactant materials is from 0.5-15 % by weight of the composition, preferably from 1 to 12 %, more preferred from 2 to 10 %, most preferred from 3 to 8 %.

It is also possible, and sometimes preferred, to include an alkali metal soap of a mono- or di-carboxylic acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. For example the sodium, potassium, ammonium and alkanol amine soaps of these acids can be used. Preferably the level of soap in compositions of the invention is from 0.1 to 5 % by weight of the composition, more preferred from 0.2 to 3%, especially preferred from 0.5 to 2%.

Also possible is the use of salting out resistant active materials such as for example described in EP 328 177, especially the use of alkyl poly glycoside surfactants such as for example disclosed in EP 70 074. Also alkyl mono glucosides may be used.

The compositions optionally also contain electrolyte in an amount sufficient to bring about lamellar structuring of the detergent-active material. Preferably

the compositions contain from 0.1% to 60% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included.

It is preferred that compositions according to the present invention include no or low levels of detergency builder material selected from STP and zeolites. Preferably the level of these builder materials is less than 20 % by weight, more preferred less than 5 %, most especially preferred less than 1 % by weight, most preferably compositions of the invention are substantially free from these builder materials.

For some purposes, it may be advantages to include some other builder materials in compositions of the invention. In this context it should be noted that some detergent active materials such as for example soaps, also have builder properties.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates and silicates, examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates and silicates.

~~Examples of organic detergency builders, when present,~~
include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilitriacetic acid, oxydisuccinic acid, melitic acid, benzene

polycarboxylic acids, CMOS, tartrate mono succinate, tartrate di succinate and citric acid.

5 Products according to the invention, preferably are used for the cleaning of surface areas, preferred embodiments of the invention are all purpose cleaners, liquid abrasive cleaners and bleach liquids.

10 All purpose cleaners of the invention, preferably contain from 1-15 % by weight of surface active ingredients, more preferred from 2-14 %, most preferred from 3-13 %. Preferably the surface active materials are selected from the group of anionic surfactant materials and nonionic surfactant materials, or mixtures thereof.
15 Preferably mixtures of anionic surfactants of the alkyl aryl sulphonate and/or primary alkyl sulphate type are used in combination with nonionic materials which are alkoxylated fatty alcohols or alkylpolyglycosides and fatty acid materials or their soaps.

20 The viscosity of all purpose cleaners in accordance with the invention is preferably from 40 to 1,800 mPas at 21 s-1, more preferred from 45 to 1,500, most preferred from 50 to 1,200.

25 The pH of the compositions is preferably from 4-13, more preferred from 6-12, most preferred from 8-11.

30 Liquid abrasive cleaners in accordance with the invention preferably comprise from 1-15 % by weight of surface active ingredients, more preferred from 2-14 %, most preferred from 3-13 %. Preferably the surface active materials are selected from the group of anionic surfactant materials and nonionic surfactant materials,
35 or mixtures thereof. Preferably mixtures of anionic surfactants of the alkyl aryl sulphonate and/or primary

alkyl sulphate type are used in combination with nonionic materials which are alkoxyated fatty alcohols and/or alkylpolyglycosides and fatty acid materials or their soaps.

5

In addition to these surface active ingredients, liquid abrasive cleaners will comprise solid particles for polishing and abrasion. Preferably a substantial proportion (say more than 50 %) of the insoluble solid particles is of small particle size, preferably not larger than 10 micrometer.

10

Examples of these materials are calcites and solid particles of potassium sulphate, silica, bicarbonate, alumina, borax, calcium carbonate, magnesium carbonate and feldspar. Preferably calcite is used.

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Preferably the level of abrasive material is from 2-70 % by weight of the composition, more preferred from 10- 60 %, most preferred from 20-50 %. Especially preferred is the use of calcite abrasives.

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The viscosity of liquid abrasive cleaners in accordance with the invention is preferably from 300 to 2,500 mPas at 21 s⁻¹, more preferred 400-2,000, most preferred 500-1,500.

25

The pH of the compositions is preferably from 6-14 more preferred from 7-12, most preferred from 8-11.

30

Liquid bleach compositions of the invention will comprise one or more bleaching ingredients such as for example chlorine bleaches, peroxy bleaches, persulphate bleaches or hydrogen peroxide. The robustness of the composition will be provided by a lamellar structure of surface active ingredients. Preferably the level of

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surface active ingredients will be relatively low, say from 0.1 to 10 % by weight of the composition, more preferred from 0.5 to 8 %, most preferred from 1.0 to 6%.

5

The level of bleach ingredients preferably corresponds to from 0.1-25 % by weight of the composition of available active chlorine and/or hydrogenperoxide, more preferred from 0.5-20 %, most preferred from 1-10%.

10

The viscosity of liquid bleach compositions in accordance with the invention is preferably from 10 to 1,000 mPas at 21 s⁻¹, more preferred 30 to 500, most preferred 80-200.

15

The pH of the compositions is preferably from 2-14 more preferred from 4-12, most preferred from 6-11.

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In addition to the bleach ingredients it is preferred that bleach compositions of the invention also comprise one or more bleach stabilising agents. Especially preferred for this purpose are phosphonates and stannates. Phosphonate bleach stabilisation materials are available under the trade-name Dequest (ex

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Monsanto).

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, fabric softeners such as clays, amines and amine oxides, lather depressants, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent

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agents, perfumes, enzymes such as proteases, amylases and lipases (including Lipolase (Trade Mark) ex Novo),

anti-redeposition agents, germicides and colourants.

Compositions of the invention may be prepared by any conventional method for the preparation of liquid
5 detergent compositions. A preferred method involves the dispersing of the deflocculating polymer ingredient in water before the formation of a lamellar droplet structure for example before the addition of the detergent active materials thereto. Especially suitable
10 is the addition of the polymer together with the minor ingredients except for the temperature sensitive ingredients -if any- in water of elevated temperature, followed by the addition of the surfactant active materials, and builder material or other electrolyte
15 ingredients under stirring and finally cooling the mixture and adding any temperature sensitive minor ingredients such as enzymes perfumes etc.

The invention will now be illustrated by way of the
20 following Examples.

Example I

An all purpose cleaner of the following formulation, was made by mixing the polymer with the water at ambient temperature followed by the addition of the surface active ingredients and the electrolytes under stirring. Finally the remaining ingredients are added. The deflocculating polymer was added as a 33 % solution in water, this solution was easily pumpable, no processing difficulties did occur. The same composition was made without polymer. Both products were stable.

Ingredient % wt	Composition	
	A	B
anionic 1)	6.0	6.0
soap 2)	1.0	1.0
nonionic 3)	3.0	3.0
sodium carbonate	7.3	7.3
perfume 4)	0.7	0.7
preservative 5)	0.1	0.1
polymer 6)	0.25	--
water	balance	

1) Sodium salt of DOBS 102 (ex Shell)

2) Potassium coconut soap

3) Dobanol 23 6.5 EO (ex Shell)

4) GC 234 E (ex Quest)

5) formalin

6) polymer A-11 disclosed in EP 89201530.6

(deflocculating polymer of formula I, wherein q, p and r are 0, v=1, x=25, y=0, R¹ is - CO - O -, R² is absent R³ is absent, R⁴ is - C₁₂H₂₅, R⁵ is -H, R⁶ is - CH₃ and A¹ is Na. The molecular weight of the polymer is about 3.5 K).

The viscosity of the compositions was measured at 1 s⁻¹, 21 s⁻¹ and 1000 s⁻¹. The results were the following:

5	Shear rate	A	B
	s ⁻¹	viscosity in mPas	
	1	4800	2900
	21	450	290
	1000	54	38

10

These results show an increased thickening of the products even when low levels of deflocculating polymer are used.

15 Example II

compositions C, D, E and F were made as in example I

	Ingredient				
20	% wt	C	D	E	F
	anionic 1)	4.0	4.0	6.0	6.0
	soap 2)	1.0	1.0	1.0	1.0
	nonionic 3)	5.0	5.0	3.0	3.0
	sodium carbonate	7.3	7.3	10.0	10.0
25	perfume 4)	0.25	0.25	0.25	0.25
	polymer ⁶)	0.25	--	0.25	--

Compositions D and F were unstable and showed more than 10 % phase separation upon storage for 3 weeks at

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ambient temperature. Compositions C and E did not show phase separation under these conditions. This example illustrates that detergent compositions of low active level can be made more stable by incorporating therein a deflocculating polymer in accordance with the invention.

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Example III

A liquid abrasive cleaner according to the invention was made by preparing a base composition by adding the ingredients in the order as indicated in example I, followed by mixing 65 parts by weight of the base composition with 35 parts by weight of calcite under stirring

Base composition

10	Ingredient	G	H
	anionic 1)	6.0	6.0
	soap 2)	1.0	1.0
	nonionic 3)	3.0	3.0
	sodium carbonate	7.3	7.3
15	perfume 4)	7.0	7.0
	preservative 5)	1.0	1.0
	polymer 6)	0.25	--
	water	balance	
20	calcite 7)	35	35

7) MM5F (ex Mineraria Maritima)

Composition G had a viscosity of 540 mPas at 21 s⁻¹, composition H had a viscosity of 290 mPas at 21 s⁻¹. Both compositions were stable at ambient temperature. Compositions G to H were used for the cleaning of shiny stainless steel surfaces. Composition H gave a greasy look to the surface, which was disliked by the consumers. Composition G did not give a greasy appearance.

This example shows that deflocculating polymers can advantageously be used for the thickening of liquid abrasive cleaners, with the additional advantage of improved cleaning performance.

Example IV

A bleach composition was prepared by preparing a base composition by the method as described in example I, followed by the addition of the peroxide ingredient. All percentages indicate the amount of ingredients in the final composition.

Ingredient (% wt)	K	L	M	N
DOBS 102		10.0		
DOB23-6.5EO		3.0		
Prifac 7901 ⁸⁾		1.0		
Dequest 2060S ⁹⁾		0.15		
Sodium sulphate		7.3		
hydrogen peroxide	5.0	5.0	--	--
available chloride ¹⁰⁾	--	--	1.0	1.0
polymer ⁶⁾	0.3	--	0.3	--
water		balance		

⁸⁾ Fatty acid soap (ex Unichema)

⁹⁾ bleach stabiliser (ex Monsanto)

¹⁰⁾ added as hypochlorite.

The pH of the compositions was adjusted with NaOH to 8.25. All compositions were physically stable, although some chemical instability due to decomposition of the bleach was noted for compositions K and L. Composition K had a viscosity of 269 mPas at 21 s⁻¹, composition L had a viscosity of 173 mPas. Composition M had a viscosity of 268 mPas, the viscosity of composition N was 191 mPas.

This example indicates that deflocculating polymers can advantageously be use for the thickening of liquid bleach compositions.

Example V

The following compositions were made as described in example I.

	Ingredient	(%wt)	P	Q	R	S
5	anionic ¹⁾			4.8		
	soap ²⁾			0.8		
	nonionic ³⁾			2.4		
	sodium carbonate			8.0		
10	perfume			0.4		
	polymer		--	0.5	0.5	0.5
	water			balance		

The polymer used in composition Q was the same as in the previous examples. Composition R contained a polymer substantially as used in the previous examples except that x=12 and the molecular weight is 3.8. Composition S contained a polymer substantially as in the previous examples except that the molecular weight is 3.8 and R⁴ is stearyl.

All compositions were physically stable. Composition P had a viscosity at 21 s⁻¹ of 120 mPas. The viscosity of compositions Q, R and S was 200, 230 and 280 mPas.

This example illustrates that an increase in viscosity can also be obtained when varying the ratio of hydrophobic monomers to hydrophilic monomers in the deflocculating polymer, or by using other hydrophobic groups.

EXAMPLE VI

An abrasive cleaner of formulation T was made as in Example I. The abrasive cleaner of formulation U was prepared by mixing the calcite into water, followed by addition of the polymer, the detergent active materials and the electrolytes followed by the addition of the remaining ingredients.

10	<u>Ingredient (% wt)</u>	<u>T</u>	<u>U</u>
	DOBS 102	3.9	3.9
	Na Prifac 7901	0.65	0.65
	Dobanol 23.6.5 EO	1.95	1.95
15	Na ₂ CO ₃	3.58	4.55
	Calcite	35.0	35.0
	polymer ¹⁾	0.5	0.32
	perfume	0.5	0.5
	water	balance	

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1) Polymer A-11 of EP 346 995 (25:1, acrylic acid/laurylmethacrylic acid polymer of MW 3,500)

Composition U had a viscosity of 1,000 mPas at 21 s⁻¹

CLAIMS

1. A detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase, said composition comprising from 0.1 to 16 % by weight of surface active materials and no or less than 20 % by weight of STP plus zeolite builder material, said composition also comprising a deflocculating polymer;

with the provisos that

- (a) when the level of surface active materials is between 12 % and 16 % by weight of the composition,

then the composition comprises no or less than 7 % by weight of STP plus zeolite builder material; and

- (b) when the composition comprises from 3 % to 12 % of a potassium alkyl benzene sulphonate, from 2 % to 8 % of a potassium fatty acid soap, from 0.5 to 5 % of a nonionic surfactant, and from 1 to 25 % of STP and/or tetrapotassium pyrophosphate, all percentages being by weight, the weight ration of said sulphonate to said nonionic surfactant being from 3:5 to 25:1, and the total amount of said sulphonate, soap and nonionic surfactant being from 7.5 to 20 % by weight,

then the deflocculating polymer does not consist solely of from 0.1 to 2% by weight of a partially esterified, neutralised co-polymer of maleic anhydride with vinylmethyl ether, ethylene or styrene.

2. Composition according to claim 1, being a liquid detergent composition.
3. Method of preparing a detergent composition according to one or more of the preceding claims, wherein the deflocculating polymer is dispersed in water before the addition of the detergent active materials thereto.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 90/01885

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C11D17/00 ; C11D3/37 ; C11D3/22		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB,A,1068554 (GENERAL ANILINE & FILM) 10 May 1967 see claims 1-13; example 4 ---	1-3
A	US,A,3457176 (J. HUGGINS) 22 July 1969 see column 4, line 63 - column 5, line 54 see column 5, line 75 - column 6, line 7; claim 1 ---	1
A	US,A,3235505 (M. TUVELL) 15 February 1966 see column 7, lines 9 - 59; claims 1, 2 ---	1-3
A	EP,A,299691 (DIVERSEY) 18 January 1989 see page 5, lines 49 - 59; claims 1-8 ---	1, 2
A	EP,A,125711 (UNILEVER) 21 November 1984 see page 8, lines 31 - 35 see page 5, lines 4 - 32; claims 1, 4; examples --- -/--	1, 2
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14 MARCH 1991	02 APR 1991	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	PFANNENSTEIN H.	

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 9001885

SA 41505

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-1068554		AU-A- 3548063 BE-A- 637821 CA-A- 722623 DE-B- 1273108 FR-A- 1403638 NL-A- 297876 US-A- 3328309	
US-A-3457176	22-07-69	None	
US-A-3235505		None	
EP-A-299691	18-01-89	US-A- 4826618	02-05-89
EP-A-125711	21-11-84	AU-B- 555110 AU-A- 2683284 CA-A- 1219509 JP-A, B 59223798 US-A- 4554099	11-09-86 25-10-84 24-03-87 15-12-84 19-11-85
EP-A-346995	20-12-89	AU-A- 3626789 AU-A- 3626989 AU-A- 3632989 EP-A- 0346993 EP-A- 0346994 JP-A- 2034699 JP-A- 2034700 JP-A- 2038500	14-12-89 14-12-89 14-12-89 20-12-89 20-12-89 05-02-90 05-02-90 07-02-90

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